COMMERCIALIZATION OF A DIRECT METHANOL FUEL CELL SYSTEM

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Abstract

This paper describes a major breakthrough in energy technology developed at the Jet Propulsion Laboratory that can be used in a wide variety of portable, remote and transportation applications without polluting the environment. The status, performance, and design considerations of the JPL non-polluting, Direct Methanol, Fuel Cell system for consumer equipment and transportation applications are reported herein. This new fuel cell technology utilizes the direct oxidation of a 3% aqueous liquid methanol solution as the fuel and air (O_2) as the oxidant. The only products are CO_2 and water. Therefore, because recharging can be accomplished by refueling with methanol, vehicles can enjoy unlimited range and extended use compared to battery operated devices requiring, recharge time and power accessibility.

INTRODUCTION

Several types of fuel cells that operate under near ambient conditions are currently under development. Hydrogen / air fuel cells that utilize a PEM (Proton Exchange Membrane) as the electrolyte or phosphoric acid liquid-electrolyte type are presently being implemented in transportation applications, e.g., for buses. Although the PEM solid polymer electrolyte fuel cells offer reduced mass, volume and enhanced simplicity, the use of H_2 as a fuel presents some practical problems, such as safety and storage system weight and volume especially for consumer and transportation applications.

Methanol is an attractive alternative to H_2 in view of its higher energy density (2 x), low cost, ease of handling and storage, and capability for distribution, Indirect methanol fuel cells using reformers to convert methanol to H_2 add complexity and cost as well as having potential for undesirable pollutants such as carbon monoxide.

This paper describes the capability of the Direct Methanol, Liquid-Feed Fuel Cell with PEM (DMLFFC/PEM) which allows the direct use of a aqueous, low concentration, liquid methanol solution as the fuel without complex on-board fuel reforming. Air (O_2) is the oxidant. The methanol and water react directly in the anode chamber of the fuel cell to produce carbon dioxide and protons that permeate the PEM and react with the oxygen at the cathode, The reactions are as follows:

Anode	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	(1)
Cathode	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	(2)
Net Reaction	$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$	(3)

The theoretical energy ca pbility of methanol as given in the above reactions is 161 ampere hours for every 32 g **(-40** cm-)^3 of methanol. The present performance is 35% of this or 1.4 kW-hr per liter of methanol.

in the present concept, methanol is stored in the fuel tank similar to gasoline. It then flows into a mixing tank to achieve a concentration of 3°/0 methanol (97°/0 water). The mixt ure then is pumped into the anode chamber. the unused methanol and water returns to the mixing tank. Water is consumed in the reaction al the anode and produced at the cathode and thus permitting a closed system. The only product other than water is non-polluting CO_2. The amount of CO_2 released would be less than that from today's internal combustion engines (ICEs) because of improved efficiency of the fuel cell system. An important advantage of this technology is that refueling can be performed in a manner similar to present gasoline refueling. Thus, with the projection of the infrastructure similar to gasoline, this technology is potentially the most practical energy source for a wide variety of transportation, and consumer applications.

CELL DESCRIPTION

A schematic diagram of a DMLFFC/PEM is shown in FIGURE 1. The existing cell employs a fine layer of platinum-ruthenium (Pt/Ru) as the anode catalyst, platinum black (Pt) as the cathode catalyst, and a polymer membrane (presently Nafion 117) as the solid polymer (PEM) electrolyte. Presently 3% aqueous solution of methanol is being used as the fuel (Higher concentrations of methanol are projected to give higher performance but are presently limited by the Nafion membrane which allows methanol to flow across to the cathode and thus inefficiently react to produce water and CO_2.) The PEM employed in the DMLFFC/PEM separates the anode (negative) and cathode (positive) chambers. The thickness of the PEM cell is on the order of 0.020" with the electrodes and separator of equal thickness.

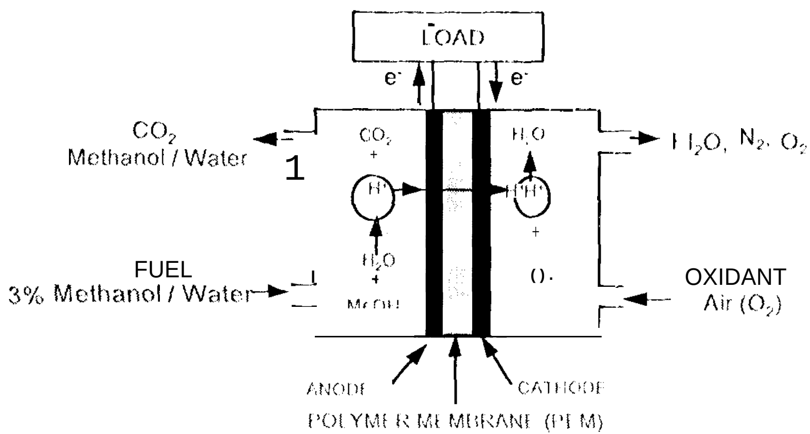

FIGURE 1. Schematic of the Direct Methanol, Liquid-Feed Fuel Cell.

The aqueous solution of methanol is fed into the fuel chamber (anode) and air circulated with a fan or under slight pressures into the cathode chamber. The air pressure selected, from ambient fan circulated air to 20 psia, depends on the application. The water produced at the cathode can be circulated back to the methanol/water reservoir or released as a vapor or liquid. The unused methanol/wafer solution is also circulated back to the reservoir where it is injected with methanol to maintain concentration. The CO_2 product is released as a gas.

TECHNOLOGY ADVANTAGES

The DMLFFC/PEM design, which uses a methanol/water in liquid form, offers numerous system level advantages over the H_2 gas-feed or methanol reformer designs. These advantages include: (a) elimination of a fuel vaporizer and its associated heat source and controls, (b) elimination of complex humidification and thermal management, (c) use of the liquid methanol/water in the dual purpose of a fuel and an efficient stack coolant, and (d) significantly lower system size, weight, complexity, and (e) operate at a temperature below the boiling point of water. Also, the solid-state PEM cell design does not suffer from the disadvantages of the phosphoric acid liquid-electrolyte cell design which is also complex, voluminous, and massive. The use of PEM eliminates the problem of troublesome shunt currents.

PRESENT PERFORMANCE

Single-cell and five-cell stacks of 5.1 cm x 5.1 cm (26 cm^2) and 10.2 cm x 15.2 cm (155 cm^2) electrode area have been operated continuously for 200 hours at 363K and intermittently by our associates at Giner Inc. for 2000 hours at 333K without noticeable degradation. The output depends on temperature and the cells have been operated over a temperature range from 283K to 363K. The advances in performance since the discovery of the technology at JPL in 1991 are shown in FIGURE 2, At the higher temperature, a 155 cm^2 exhibits 0.5 V at a continuous load of 48 Amps using 3% methanol and 20 psig air. A peak power of 39 W is achieved at 96 Amps. At 333K, a five cell 155 cm^2 electrode stack exhibited 2.3V at 23 A. With regard to response, the voltage immediately responds to changes in load.

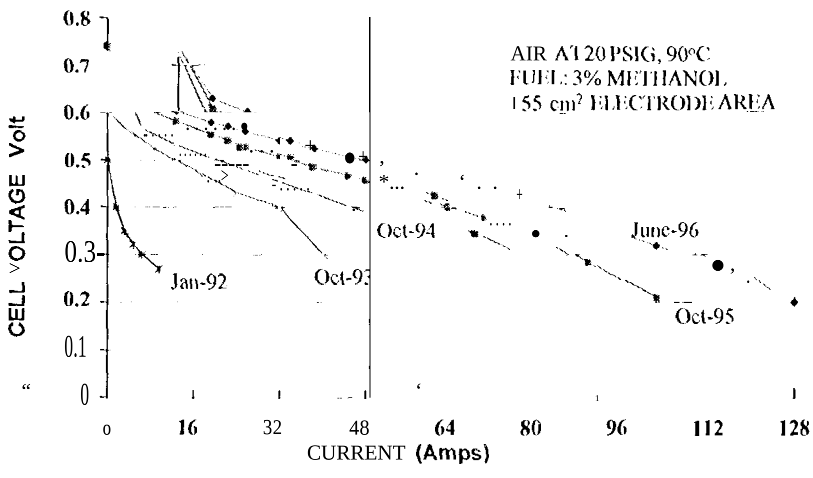

FIGURE 2. Advancements in Performance

SYSTEM ISSUES

A basic schematic of the fuel cell system is given in FIGURE 3 which operates as described above. It provides an example of a DMLFFC/PEM stack integrated into a system. An overall systems study for applications from 5 W to 5 kW has shown that with the auxiliary equipment required to maintain the controls in an integrated DMLFFC/PEM system is viable. Several factors have to be considered in designing a DMLFFC/PEM system for an application. The four subsystems including; the, Methanol/Water Feed, Thermal and Water Management, and Electronics and Controls.

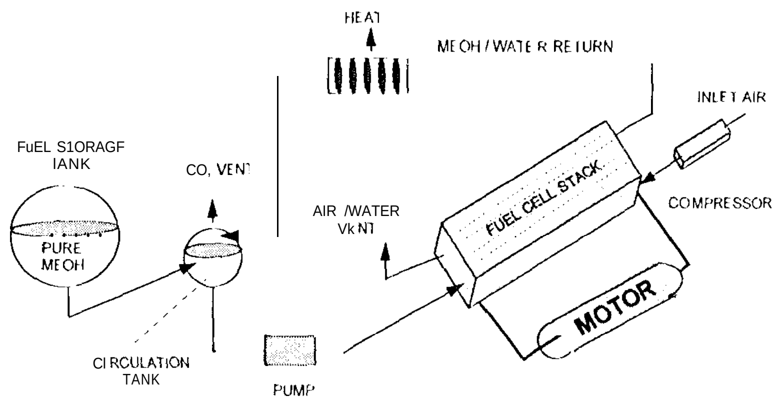

FIGURE 3. Schematic of a DMLFFC/PEM System

<u>Cell and Stack Subsystem</u>

The application will dictate the voltage, current and peak power requirements. The voltage required depends on the number of cells in series comprising the stack. The electrode area determines the current capability. The appropriate combination of voltage and current can either be supplied to the buss directly or can go provide input into a voltage converter. Keep in mind that one of the advantages of this system is that small increases in electrode area can increase current capability substantially while voltage is a function of the number of cells. Both are affected by temperature, rate of reaction, quantity and rate of oxidant, and concentration and rate Of fuel flow. Thus a balance has to be achieved for each application.

One of the key features affecting stack design is the bipolar plate (biplate) which plays three roles: it provides the electronic conduction from one cell to the other avoiding cell interconnects, it provides a flow-field for the fuel mixture and air to flow through manifolds to the appropriate electrode surface, and transmits the force from the endplates to the electrodes to maintain conductivity.

<u>Methanol/Water/O_2 Feed Subsystem</u>

This subsystem provides the mechanism for mixing, maintaining and feeding the aqueous methanol to the anode chamber. This can be done by controlling the concentration of the methanol in the mixing chamber by a methanol sensor designed for that purpose. A small pump or pressure device is used to move the aqueous fuel into the anode manifold in the stack at a constant pressure and flow rate. The unused methanol and water returning to the chamber also contains CO_2 from the anode reaction. Because the CO_2 is in the form of a gas it is separated from the liquid and released from the mixing, chamber. Although there is a potential for droplets of methanol to accompany the gas release. a filter will be employed to prevent this from d to react with the protons diffusing through the PEM. The system provides maximum power with O_2, however, adequate power is provided using air (FIGURE 4). Again, although pressurized air is desired to maximize O_2 to the cathode, the system can provide adequate power for some applications by using a simple fan to provide air flow through the flow-field and across the cathode surface. Because there is no liquid electrolyte, the cathode can be exposed to outside air. The power density of 230 mW/cm^2 at 600 mA/cm^2 (equivalent to 100 A on a 1 S5 cm^2 electrode) using air is compared to O_2 as the oxidant in shown in Figure 5.

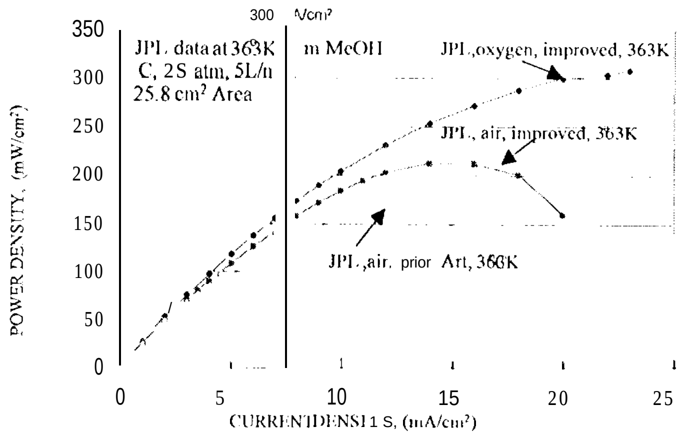

FIGURE 4. Power Performance of the DMLFFC/PEM

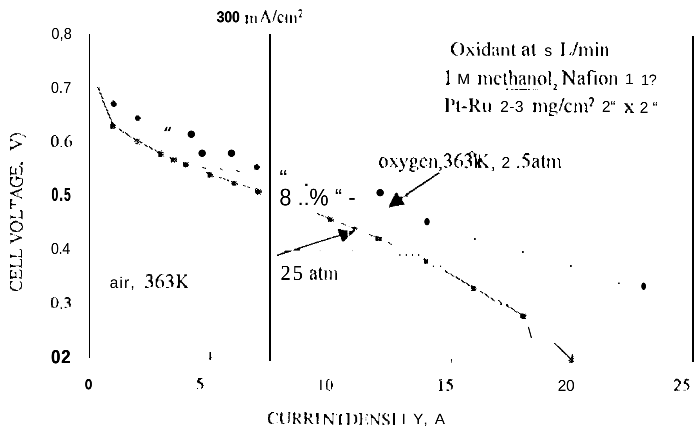

FIGURE 5. Performance of Air and oxygen

Thermal And Water Management Subsystem

Water is used in the reaction with methanol at the anode. However, as given in the reactions 1-3 above, three times as much water is produced as reacted. Water also enters the cathode chamber from two other sources; a) water dragged through the PEM along with the protons, and b) water produced in tbc cathode chamber by the reaction of methanol that also is dragged through the membrane into the cathode side. The latter product is the same as that produced electrochemically, i.e., CO_2 and water, however, this is an inefficient reaction from an energy point of view because no electrons are generated.

The water recovery and temperature of operation is used for balancing the amount of water returning to the mixing chamber, that which is vaporized and that which is released as a liquid. For example, in a transportation application water would be circulated through a radiator of the type presently in use in vehicles to maintain the constant operating temperature. Coincidentally, it is the same temperature (~373K) that is used in vehicle radiators today. in the case of a lawn mower application the water could be used to water the lawn as it is mowed. In a marine application the water in pure form from the cathode chamber could be stored for drinking or cooking. The rate and temperature at which the water is produced determines the state of the effluent and therefore the temperature of operation. The effect of temperature on performance is given in Figure 6 for air and oxygen for a five cell stack. Note that although the performance is lower, operating at a lower current will result in the same voltage output. This is the case for the two military applications described below.

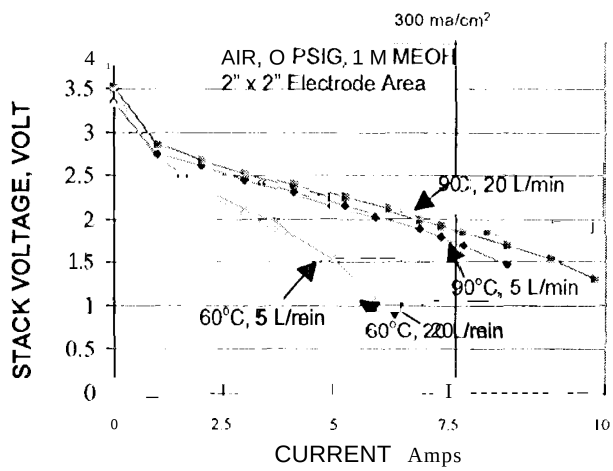

FIGURE 6. Performance of a 5 cell stack at 333K and 363K

Electronics and Controls Subsystem

Controls are needed for pumping fuel and air into the appropriate manifolds. Selection of these is dependent on the application. Sensors are required to monitor and control methanol concentration and temperature. A converter may be required to boost the voltage of a stack to the operating voltage. For example, a 110 V system using only fuel cells would require a 220 cell stack. The fuel and oxidant flow as well as continuity of the stack can be complex. As an alternative, a smaller stack of 50 cells producing 25V can be boosted to 110V with a loss in efficiency of about 10%. The electrode area would have to be increased to account for the additional current and inefficiency. However, with 0.3 A/cm^2 the increase in area would be reasonable.

PRESENT APPLICATIONS

Under the JPL 'Technology Affiliates Program, the DMLFFC/PEM technology developed at JPL has been transferred to DTI Energy, a private California company interested in the mass-scale manufacturing of fuel cells. DTI has been funding the DMLFFC/PEM development effort for transportation, stationary power and commercial applications.

In the DARPA program at JPL, Giner, and USC are involved in the development of an advanced lightweight DMLFFC/PEM system to replace the BA 5590 primary lithium battery used in defense communication equipment. This has the advantage of significantly reduced logistical issues as well as longer operational life without disassembly. A SOW fuel cell system including ancillaries will replace the 12.7 cm x 10.2 cm x 6.4 cm battery pack presently in use and allow the soldier to recharge his fuel cell power pack in the field (FIGURE 7). his system is being designed for 333K operation and the use of flowing air.

In a program for the U.S. Army, a small 4W fuel cell/ battery system for field use. This application is also to replace batteries where 6 months of field storage is required while communications are ongoing. A reservoir will be provided to store the methanol. in addition, a lithium-ion battery will be provided to provide the peak power and thus minimize fuel cell stack size (FIGURE 8). This system is being designed for 293K operation.

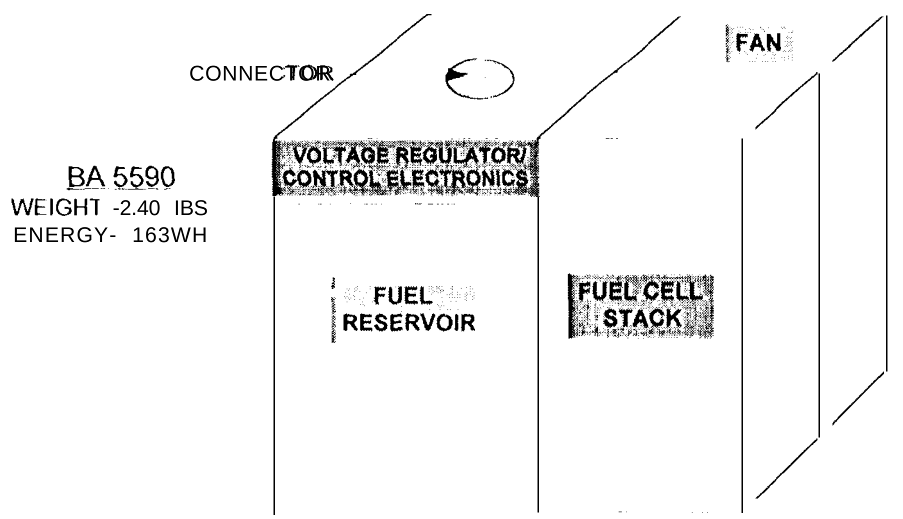

FIGURE 8. BA5590 with a DMLFFC/PEM Replacement

In a design provided by Giner Inc. a small vehicle requiring 5 kW of power could be provided with a DMLFFC/PEM system wherein the fuel cell stack is projected to be approximately 28 liters. The ancillaries associated with the operating system would add 25% to the package. The projected characteristics of a 5 kW stack that would go into a light-weight vehicle-type using state-of-art materials are shown in TABLE 1. Preliminary analysis of stack system shows that a minimum cell voltage of 0.55V and current density of 300 mA/cm^2 with a crossover loss of 10°/0 is required to achieve >300 W/kG and 300 W/l for a 500 W stack. This design point appears feasible based on performance achieved to date and the advanced development tasks planned for this program. The data shown in TABLE 1 were developed for a 5 kW DMLFFC / PEM with 91 cells of active area 316 cm^2/ccl].

PROJECTED PERFORMANCE

‘1 ‘he present electrochemical efficiency (product of voltage efficiency and fuel efficiency) of the laboratory cells is about 35% when air is used as the oxidant, i.e., the voltage of 0,5 V together with the methanol crossover accounting for 20% of the current. It is expected that with a new membrane that restricts methanol crossover, higher methanol concentration, and improved electrode designs and catalysts, higher voltage and current, efficiencies approaching 50°/0 levels are achievable, i.e., with 0.6V/ ccl] and <1 0°/0 crossover. USC has reported that a membrane is available that restricts methanol crossover to 5%.

Finally, It is projected that the cost can also be reduced with the new low cost membranes, lower platinum loading and low cost biplates all of which are under development. Further, since Platinum is recoverable, a system for trading in older fuel ccl] stacks is also possible thus lowering the cost.

‘l’All] .E 1: Projected [characteristics of Proposed 5kW Stack

GIVEN	
System Output power (kW)	5
System Output Voltage (V)	50
Overall Thermal Efficiency (Fraction)	0.4
Cell Current Density (mA/cm^2)	300
Minimum Single Cell Voltage, (V)	0.55
Single Cell Active Area (cm^2)	316
Crossover (1 0%) Current Density (ma/cm^2)	30
Methanol/O_2 Reaction (V)	1.25
RESULTS	
No. of Cells in Electric Series	91
System Weight (kg)	14.7
System Volume, (Liters)	14.5
Length of Stack (cm)	38
Height of Stack, (cm)	19
Width of Stack, (cm)	19
Power Density (W/Liter)	344
Specific Power (W/kG)	365

SUMMARY

Significant performance has been demonstrated by a non-polluting, easily refuelable Direct Methanol, Liquid-Feed Fuel Cell with PEM that has application in a number of military, commercial and vehicular applications. Systems models have shown the capability for meeting applications from 4 W to 5 kW and beyond, The present stack performance efficiency of 35% has been demonstrated with 50% realistically projected.

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